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UV-laser photodissociation of azulene at 325 nm is reported. The photodissociation reaction occurs by a two photon absorption process producing acetylene. The quantum yield for acetylene produced by irradiation of neat azulene and azulene/argon mixtures is reported. The quantum yield of acetylene produced after irradiation of neat azulene at its normal vapor pressure is approximately $(5.85 \pm 1.46) \times 10^{-6}$.

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Photodissociation Of Azulene Under UV-Laser Irradiation At 325 nm

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Abstract

UV- laser photodissociation of azulene at 325 nm is reported. The photodissociation reaction occurs by a two photon absorption process producing acetylene. The quantum yield for acetylene produced by irradiation of neat azulene and azulene/argon mixtures is reported. The quantum yield of acetylene produced after irradiation of neat azulene at its normal vapor pressure is $\sim(5.85 \pm 1.46) \times 10^{-6}$.

Introduction:

Azulene is attractive to many researchers because of its characteristic photophysical properties and is used in collisional energy transfer¹, spectroscopic and photophysical²⁻³ studies. Fast internal conversion process from the excited electronic states produces vibrationally highly excited molecules in the ground electronic state.⁴⁻⁶ Azulene in its excited electronic states, S_1 and S_2 , internally converts to S_0 with lifetimes of picoseconds and nanoseconds, respectively, and quantum yields close to unity.⁷⁻⁸ Excitation to higher states like S_3 or S_4 rapidly converts to S_2 which is then followed by internal conversion to S_0 .²

Azulene, in its vibrationally highly excited ground electronic state has been used extensively by several groups to study the collisional energy transfer process.¹ The collisional deactivation of excited azulene by various bath gases was studied by Hippler, Troe and co-workers⁹⁻¹² using time-resolved ultraviolet absorption spectroscopy (UVA).¹³⁻¹⁵ Barker and co-workers using their time-resolved infrared fluorescence method (IRF)¹⁶ performed similar studies.¹⁷⁻²² Jalenak et al.²³ studied the vibration to vibration energy transfer from highly excited azulene to CO_2 by diode laser absorption spectroscopy. Hassoon et al.²⁴ used azulene as the hot donor in their collisional induced sensitization method for studying super strong collisions. Classical trajectory simulation techniques for obtaining collisional energy transfer parameters have been applied by Gilbert et al.²⁵ to azulene with a series of monatomic bath gases.

Recently, the unimolecular isomerization of azulene to naphthalene under thermal and selective photoexcitation was studied by Troe et al.²⁶⁻²⁷ The thermal isomerization was studied in shock waves over the range of 1300-1900 K²⁶. Single and multiphoton UV excitation with a nanosecond pulsed excimer laser at 193, 248²⁷ and 308nm¹⁰ were used in the photoisomerization study. It was

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shown that the isomerization process is a "clean" unimolecular reaction with 1:1 conversion of azulene to naphthalene. Based on the thermal isomerization results and fit to an RRKM calculation, the specific rate constants, $k(E)$, for the unimolecular reaction were constructed. By comparing the measured rate constants from the photoexcitation experiment and those from the RRKM calculation, these workers concluded that only at the short wavelength, 193nm, does azulene undergo a one-photon photoisomerization. However, in the longer wavelengths, 248 and 308 nm, two- and three-photon excitation is needed.^{10,27}

In the present work we found that UV-excitation can lead also to photodissociation of azulene in a two-photon absorption process. Typically, photodissociation of organic molecules does not occur under one photon irradiation unless very short wavelengths, 193 nm, are used.²⁸⁻²⁹ On the other hand, two or multiphoton absorption processes result in dissociation over a wide range of wavelengths. Generally, UV multiphoton excitation leads to ionization of gaseous molecules, however, if very fast internal conversion occurs, high vibrational excitation of the molecules in their ground electronic state can be achieved. Dissociation, unimolecular isomerization and collisional energy transfer can then be studied.

Experimentally, two methods are used in these studies: (a) time-resolved methods using intense, ultrashort pulses for both excitation and probe or (b) continuous-wave methods measuring yields as a function of light intensity and gas pressure. The UV multiphoton dissociation of toluene, ethylbenzene and n-butylbenzene was studied by Nakashima et al.³⁰ Using 193 nm excitation under conditions where the one photon dissociation process was completely quenched by collisions, they found that the yields of benzyl radical produced increased with the square of the laser intensity. On going to higher intensities, the yield decreased which was attributed to the destruction of benzyl by absorption of a third photon. Troe, Hippler et al.³¹ studied the multiphoton dissociation of toluene, ethylbenzene and cycloheptatriene. The yields of benzyl and methyl radicals and other final products were measured as a function of the laser intensity and the bath gas pressure. They also found that the observed yields indicated a two-photon absorption process. However, they suggest a spontaneous fragmentation of the highly excited radicals produced by the initial two-photon excitation of the parent molecule instead of the absorption of a third photon which was suggested in the former work.

In this work, even with the comparatively modest laser intensities used, we found that azulene excited at 325 nm dissociates. Acetylene is the major final product with at least two other minor products being formed.

Experimental

Gas samples of pure azulene at its room temperature vapor pressure (near 10 mTorr) and diluted with argone as inert bath gas (up to 20 torr) were irradiated by laser light at 325nm. A helium-cadmium cw laser (Omnichrome, Series 74) was used with maximum power of 40 mW and beam

diameter of 1.2 mm. The output power of the laser beam was monitored by a calibrated Scientech 365 power meter with the UV-360001 calorimeter head. The irradiation cell was a pyrex cylinder (22.5 cm length, 1.3 cm inside diameter) outfitted with two Brewsters angle quartz windows.

The irradiation yield of acetylene was measured as a function of the laser intensity and as a function of the added inert gas pressure at the same intensity. Neutral density filters were used to vary the laser light power from 3 to 26 mW. The amount of azulene in the irradiation cell was kept constant and equal to its vapor pressure during the irradiation time by leaving the sample holder open to the cell. Typical irradiation times were one hour. In order to check the type of the absorption process the laser beam was expanded using a broadband beam expander (Ealing, expansion ratio X5).

After irradiation, the samples were analysed by HP 5890 gas chromatograph equipped with a flame ionization detector and 3392A integrator. Quantitive analysis has been done only for the acetylene produced using a 12 ft x 1/8 in stainless steel column packed with Chromosorb 104, 80/100 mesh (Alltech Associates). The column temperature maintained at 100 C with a He carrier gas flow rate of 30 ml/min. Retention time of 1.6 min was obtained.

Azulene (Aldrich, >99%) was purified by pumping several times over the sample holder. The argon (Matheson, >99.998%) was used without further purification, but contained a small quantity of acetylene. Blank runs at each pressure of argon were used in order to correct for this impurity.

Results and Discussion

The linear dependence of the relative amounts of acetylene produced in the irradiation of neat azulene vapor pressure as a function of the square of the laser intensity are shown in figure 1. The acetylene produced increases linearly with the square of the laser intensity. When the laser beam was expanded by a beam expander no acetylene was detected. Moreover, using collimated light with a 10 nm bandwidth centered at 325 nm from a 200 W high pressure mercury lamp with intensities comparable to those of the laser, no acetylene was observed.

Figure 2 shows the measured quantum yields of acetylene produced by the photodissociation as a function of the pressure in the cell. The quantum yields decrease with increasing pressure as expected in photolysis experiments in the gas phase due to collisional deactivation. At pressures higher than 10 torr the quantum yield becomes too small to measure. The measured quantum yield at the normal vapor pressure of azulene is $(5.85 \pm 1.46) \times 10^{-6}$. The large error (~25%) in evaluating the quantum yield value is a result of the difficulties of measuring accurately the small amount of laser intensity absorbed by the azulene which are needed to calculate the number of photons absorbed.

The dependence of the acetylene yield on the square of the laser intensity, indicates a two-photon absorption process. Our proposed mechanism of the process follows earlier studies on toluene and other molecules.³⁰⁻³¹ Excitation of the azulene by the first photon produces a hot molecule in high vibrational state in the ground electronic state after very fast internal conversion. Hot molecules

show broad, strong absorption spectra in the UV region ¹¹⁻¹² and easily absorb a second photon leading to dissociation.

The present experiment does not indicate the dynamics of the primary processes. Intermediate radicals and fragments are probably formed producing acetylene as the final product. Time-resolved experimental methods with ultrashort intense laser pulses are needed to evaluate the rate constant for the dissociation process from the observed data. In the GC analysis of the irradiated samples we can see another three products in addition to the isomerization product - naphthalene. One of these products was identified as phenylacetylene, however the amounts of phenylacetylene detected were very small relative to acetylene (less than 1: 5) making an accurate quantitative determination impossible. The other two products were obtained in very small amounts also and were not identified.

The possibility of one photon isomerization of azulene to naphthalene which then absorbs the second photon and dissociates, has very low probability. It was shown ^{10,26-27} that one photon isomerization does not occur at 308 and 248 nm excitation due to the low energy of the photon. Moreover, the acetylene was obtained at pressures up to 10 torrs, where collisional deactivation is expected to cool any hot naphthalene produced.

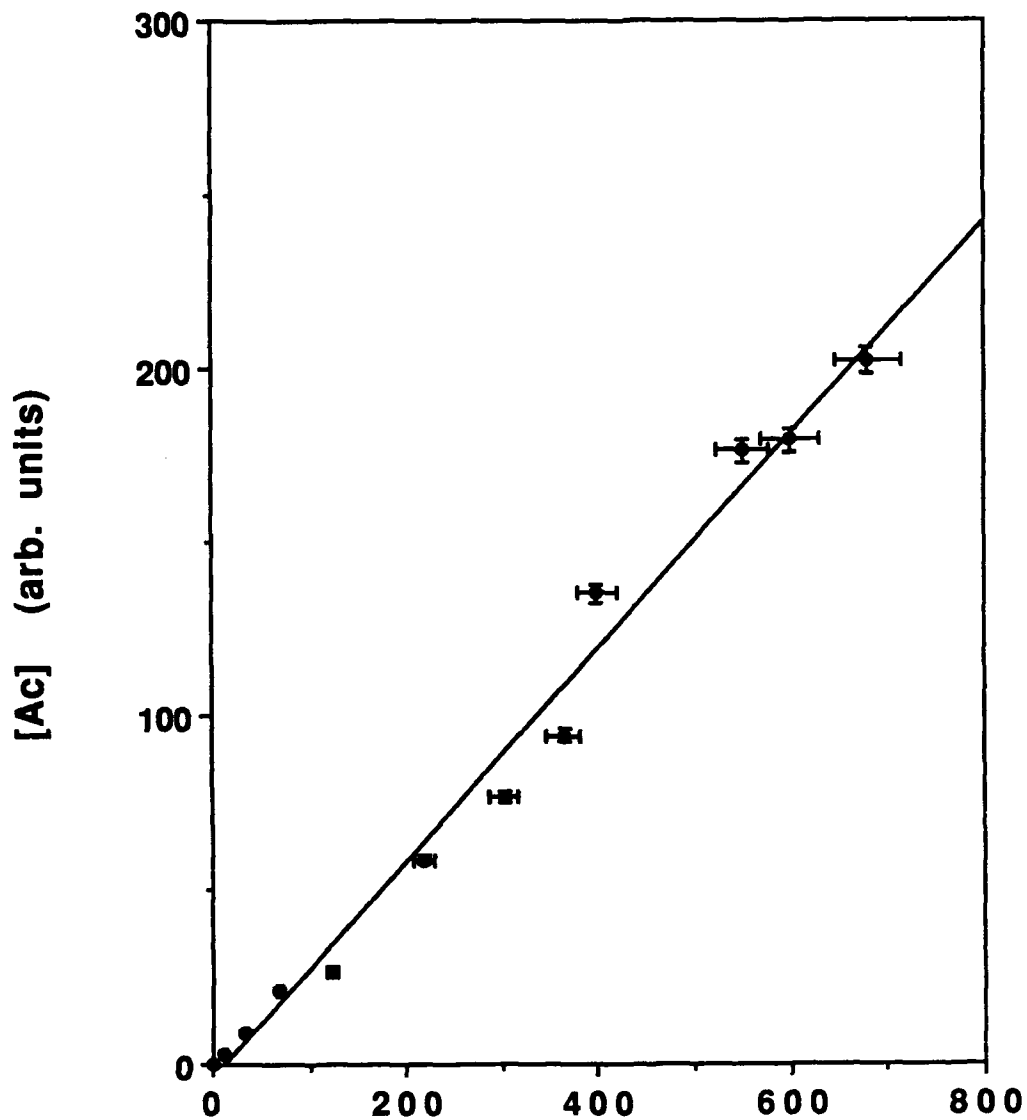
Conclusions

The photodissociation of azulene by UV multiphoton excitation occurs at relatively long wavelength (325 nm) and low laser intensity. From the dependence of the yields of acetylene as a function of the laser intensity, the photodissociation is a two-photon absorption process. Time-resolved experiments are needed to learn more about the photodissociation dynamics and for evaluation of rate constants of the process.

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Fig. 1



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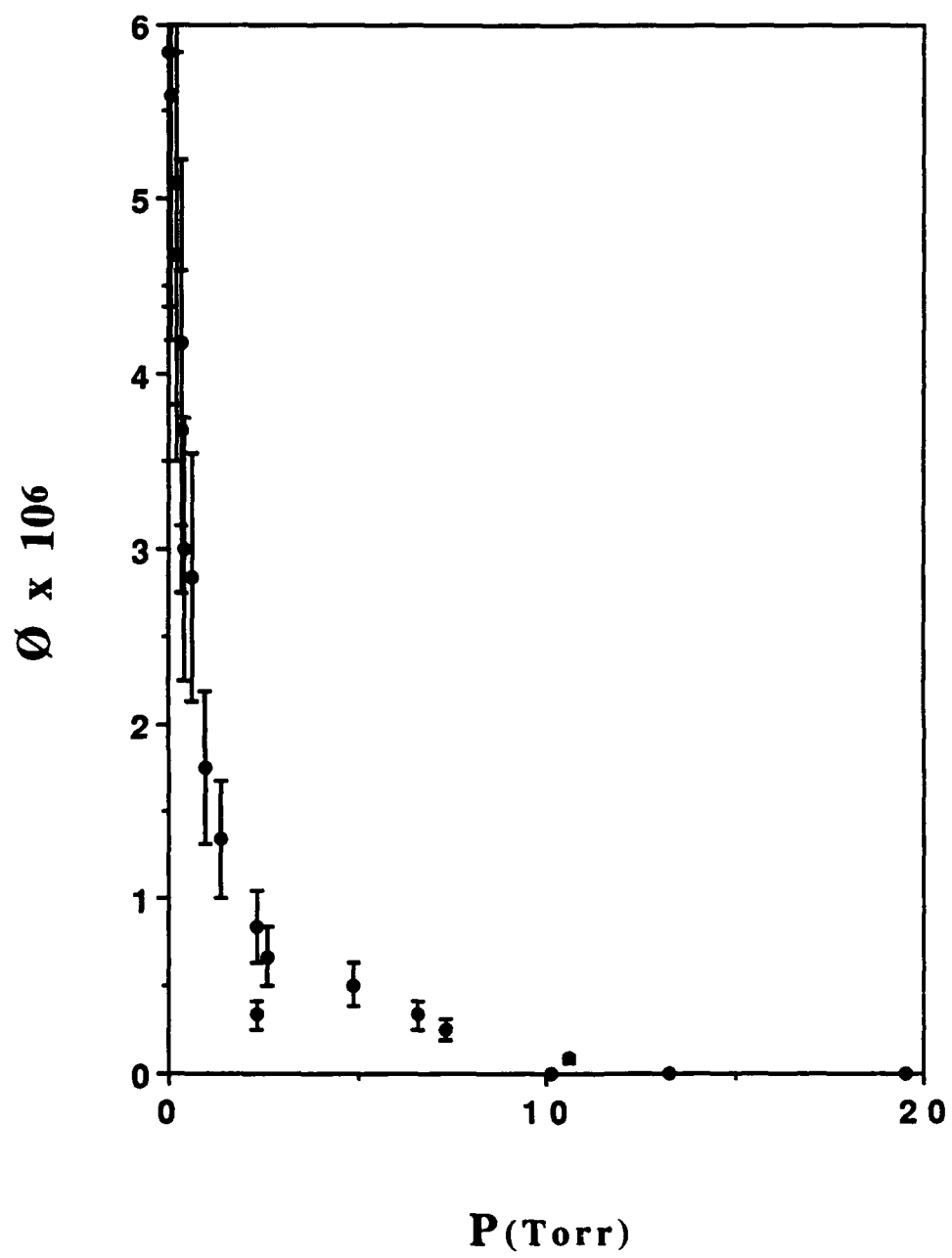
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Figure Captions

Figure 1 : The relative amounts of acetylene produced after irradiation of azulene as a function of the square of the laser intensity.

Figure 2 : The quantum yields of acetylene produced as a function of the added bath gas pressure. The quantum yields were calculated as the number of acetylene molecules produced per photon absorbed by the azulene samples.

Fig. 2



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